VARIATIONS IN GLASS COMPOSITION IN AN OPERATING FURNACE

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The change in the Fe(II) $\rightleftarrows$ Fe(III) redox equilibrium in the $Me_2O - MeO - Al_2O_3 - SiO_2$ system is studied in conditions of complex variation of diversely acting parameters affecting sheet glass production (the glass matrix basicity, reduction potential of the batch, and Fe_2O_3 content).

The replacement of costly imported materials with less expensive local materials and increased application of glass cullet usually results in an increased content of iron oxides in the glass composition. As manufacturers replace the raw materials introduced into the batch, they simultaneously try to improve the melting and working qualities of the glass melt, the quality of finished glass, and the technical and economical parameters of the glass production technology [1 – 3].

The main attention in doing so is usually focused on the variation and correction of the content of basic oxides (SiO_2, Al_2O_3, CaO, MgO, Na_2O, K_2O) in the glass composition. The spontaneous change in the content of impurity oxides (including Fe_2O_3) occurring in this case can hamper the glass-melting process and impair the technical and economical parameters of glass-melting furnaces.

There are numerous publications which discuss the behavior of iron oxide in the melting of multicomponent glasses of the $SiO_2 - Al_2O_3 - MeO - Me_2O$ system. These data mostly relate to the large-scale production of packaging and heat-absorbing glass [4, 5] which contains over 1.0 and 0.3% Fe_2O_3, respectively. However, data on the effect of heterovalent forms of iron on the production of glass containing less than 0.1% Fe_2O (glassware, clear packaging and construction glass) are scarce, uncoordinated, and contradictory, which calls for further research.

For the purpose of decreasing the leaching of glass in the course of continuous production, the Avtosteklo production company in 1998 replaced the glass composition used in continuous rolling (CR) by a composition used in vertical flow (VF) glass production. This process was accompanied by the introduction of new types of raw materials (feldspar concentrate and dolomite [3]). A preliminary analysis of expediency of this conversion to a new glass composition (Table 1) showed that on substitution of the VF glass for the CR glass, the amount of fluxes (the total content of oxides of alkaline and alkaline-earth metals) increases by 1.55%, mostly due to a decrease in the total content of the high-melting components ($SiO_2 + Al_2O_3$). An increase in the content of Al_2O_3 from 0.3 to 1.9% takes place due to the use of a complex mineral material, namely, the feldspar concentrate in the batch used for the vertical flow glass production. The introduction of this concentrate makes it possible to decrease the soda content in the batch by 12.9%. The use of dolomite promotes a decrease in the chalk content in the batch, and in this case magnesium oxide is additionally introduced to the glass.

The data on the measurement of viscosity of the above mentioned glasses made in laboratory conditions (Table 2) [3] revealed that the viscosity at the temperature of fining ($\log \eta = 2$) is equal for both compositions: the safe molding interval improves. All this indicates that the VF glass is more technologically suitable than the CR glass.

[1] Avtosteklo Production Company.

TABLE 1

Glass	Preassigned composition, %								Batch composition, kg per 100 kg of glass						
	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	Na_2O	SO_3	$Na_2O +$ MeO	sand	chalk	dolomite	soda	feldspar	sodium sulfate	coal
Continuous rolling	74.50	0.05	0.30	8.70	0.15	15.50	0.80	24.35	72.05	16.31	–	26.52	–	1.33	0.07
Vertical flow	71.60	0.10	1.90	6.90	4.00	15.00	0.50	25.90	65.99	0.93	19.63	23.10	8.70	1.84	0.13

However, the results obtained in glass melting in a tank furnace with a capacity of 130 tons/day differed from the expected values (Table 2) [3]. In spite of the increased flux content in the composition of VF glass, the maximum temperature of its melting increased by 40°C whereas the system efficiency and the degree of homogeneity of the glass melt were maintained at a preassigned level.

The obtained results can only be explained by a detailed consideration of the behavior of Fe_2O_3 in the melt. According to the contemporary concepts, iron oxide exists in glass in the state of redox equilibrium

$$Fe(II) \rightleftarrows Fe(III) \qquad (1)$$

whose position is determined by the redox potential of the glass melt, i.e., its basicity [6]. On the one hand, the latter depends on the content of oxidizing (reducing) impurities in the material, i.e., on the redox potential (RP) of the batch and the glass composition. On the other hand, this parameter is related to the glass-melting conditions and is determined by the partial oxygen pressure above the melt (the gas medium composition in the tank furnace) and the time-temperature conditions of melting.

The redox characteristics of the raw materials serve for preliminary evaluation of the state of equilibrium (1) in the glass melt based on the variation in the rated value of the batch RP. The method for the calculation of redox potential is simple and widely used in glass technology.

The effect of the glass composition on the equilibrium of the heterovalent forms of iron in melts is mostly determined by the ratio between the acid (SiO_2, Al_2O_3) and basic (Na_2O, CaO, MgO) oxides [6].

Some authors report a shift of the redox equilibrium (1) toward the formation of iron with a lower oxidation level, when the share of acid oxides (i.e., the glass acidity) increases. An increase in the content of basic oxides (an increase in basicity and, accordingly, a decrease in acidity of glass) changes the direction of the redox reaction (1) to the opposite direction. It is established that as the partial pressure of oxygen increases and the melting temperature decreases, the redox equilibrium (1) shifts toward a higher level of iron oxidation.

However, virtually all papers consider the effect of only one of the above listed reasons on the behavior of iron oxide

in the glass melt. And yet, there are different factors which have an integrated effect on the glass melting process and determine the dynamics of $Fe(II) \rightleftarrows Fe(III)$ equilibrium in the melt.

In order to investigate this phenomenon, it is necessary to select a reference parameter which could make it possible to evaluate quantitatively the variations in the oxidizing potential of glass melt depending on the integrated effect of different factors.

Taking into account the similarity of the redox processes taking place in aqueous solutions of chemical compounds and in silicate melts, as well as the fact that iron is present in silicate melts in the state of redox equilibrium, we chose the following expression for indirect determination of the glass melt basicity:

$$d_{Fe(II)} = \frac{w_{Fe(II)} \times 100}{w_{Fe(II)} + w_{Fe(III)}} \qquad (2)$$

where $w_{Fe(II)}$ and $w_{Fe(III)}$ are the weight fractions of Fe(II) and Fe(III), respectively, in the melt.

This expression which we termed the indicator of glass basicity makes it possible to determine the fraction of bivalent iron $d_{Fe(II)}$ in the glass melt and indirectly evaluate the total effect of different technological parameters (composition of raw material, batch, and glass, temperature of glass melting, content of iron oxide, etc.) on the actual variation in the glass melt basicity.

Expression (2) has the following advantages:

direct presence of the indicator, namely, iron oxide in the state of redox equilibrium in glass;

simplicity of the method used to determine the total content of ferric $w_{Fe(III)}$ and ferrous $w_{Fe(II)}$ oxides; the total content of Fe_3O_4 determined by the photocalorimetric method corresponds to the total content of FeO + Fe_2O_3 (the content of FeO in glass was determined by optical spectroscopy in compliance with the recommendations given in the Regulations for Operation of Glass Factories).

A drawback of the method consists in the error resulting from determination of Fe(II) and Fe(III) content by the existing methods.

Table 3 presents the main phases of gradual conversion of the industrial technology from the CR glass to the VF glass. The technology was modified in the conditions of con-

TABLE 2

Glass	Technological properties					Actual technological parameters		
	temperature of characteristic viscosity points at		temperature of upper crystallization limit, °C	safe molding interval, °C	glass homogeneity, °C	maximum melting temperature, °C	gas consumption, m³/h	specific output of glass melt, kg/m³ per day
	$\log \eta = 2$	$\log \eta = 3.5$						
Continuous rolling	1450	1040	1070	30	1.5 – 2.0	1470	1600	720 – 760
Vertical flow	1450	1100	925	175	1.5 – 2.0	1510	1680	720 – 760

tinuous production and was accompanied by a parallel introduction of new types of material (i.e., feldspar concentrate and dolomite) to the batch. Table 3 shows that the content of all oxides (except for SiO_2) in glass significantly changed. In the final variant (VF glass), the total content of the high-melting oxides ($SiO_2 + Al_2O_3$) decreased by 1.33% due to an increase in the total flux content, which points to the increased basicity of the VF glass, as compared to the CR glass.

The estimated RP of the intermediate batch compositions (the calculation was performed using the method in [6]) exhibits fluctuating variations but, as a whole, retains the general tendency for a decrease in the carbon number from 11.72 (CR glass) to 9.09 (VF glass). This is evidence of an increase in the redox potential of the VF glass batch compared to the CR glass batch. The fluctuations in the redox potential of the batch in transition from CR glass to VF glass are related to the adjustment of the fining conditions of the melt, which required an increase in the glass-melting temperature (Table 2). The total light transmission (Table 3) decreases by 1.6%, i.e., from 88,4% in CR glass to 86.8% in VF glass. This is due to an increase in the Fe_2O content in VF glass by 18% (up to 0.071%), compared to CR glass (0.060%). It should be noted that the variations in the Fe_2O_3 content in the considered process satisfy the requirements of the Operating Regulations.

All this is evidence of the existence of at least several groups of opposing factors which influence the variations in the RP of the glass melt and, consequently, the equilibrium state of the heterovalent forms of iron. The first group of factors includes the variations in the content of basic oxides in the glass composition, which increases the glass basicity. The second group of factors is associated with the redox parameters of the raw materials, which determine the decrease in the RP of the batch. The effect of the latter factors is intensified by an increase in the total content of Fe_2O_3 and increase in the maximum glass-melting temperature (the third group of factors).

The actual direction of the shift in the redox equilibrium (1) can be found using the indicator of glass basicity, which characterizes the variation in the content of Fe(II) in glass produced by the above factors. The results cited in Table 3 indicate that the Fe(II) content in all the intermediate and final compositions of VF glass varied from 32.6 to 42.6% and was significantly higher than the average Fe(II) content (25.6%) in the initial composition of CR glass. Hence it follows that, in the end, the content of Fe(II) increases half as much again the average value of CR glass (25.6%), up to 37.5% (VF glass), which is evidence of a decrease in the glass melt basicity.

As can be seen in Table 3, the correlation between the Fe(II) content and the RP of the batch is not always satisfied. In our opinion, this is due to the presence of uncontrolled oxidizing (reducing) impurities and indicates that it is preferable to monitor the glass-melting process based on the glass basicity indicator.

The result of the action of heterogeneous technological factors is a decrease in the melt basicity, which produces an increase in the absolute content of ferrous oxide (Table 3). This, in turn, causes a decrease in diathermancy of the glass melt, which determines the need to increase the maximum glass-melting temperature in order to stabilize the glass melting process.

In order to facilitate the glass melting process and to maintain the tank furnace operating parameters at preas-

TABLE 3

Phase in the replacement of glass composition	Component content (from analysis), %								Batch RP	Integral light transmission per 1 cm thickness, %	Content of Fe(II), %	$d_{Fe(II)}$*, %
	SiO_2	Al_2O_3	CaO	MgO	Na_2O	SO_3	Fe_2O_3	$SiO_2 + Al_2O_3$				
Prescribed continuous rolling phase	74.50 ± 0.3	0.30	8.70 ± 0.2	0.15	15.50 ± 0.2	0.80	0.050	74.80	–	–	–	–
Actual continuous rolling phase	74.50	0.13	8.68	0.21	15.49	0.44	0.060	74.63	11.72	88.4	0.0124	29.5
Intermediate compositions	74.50	0.12	8.80	0.15	15.48	0.54	0.064	74.62	11.72	88.2	0.0117	26.1
	74.38	0.21	8.66	0.32	15.51	0.62	0.045	74.49	11.72	88.2	0.0124	39.5
	74.15	0.65	8.18	1.00	15.24	0.55	0.060	74.80	10.80	87.2	0.0155	37.0
	73.35	0.98	3.02	1.95	15.43	0.46	0.052	74.33	10.80	87.4	0.0155	42.6
	72.90	1.33	7.47	2.74	15.17	0.42	0.070	74.23	11.25	86.8	0.0171	34.9
	72.15	1.46	7.36	3.11	15.17	0.42	0.064	73.61	11.47	86.8	0.0171	38.2
	71.50	1.66	7.27	3.60	15.20	0.46	0.068	73.16	9.09	86.9	0.0163	32.6
Prescribed vertical flow phase	71.57	1.73	6.90	3.91	15.21	0.40	0.071	73.30	9.09	86.8	0.0179	37.5
Actual vertical flow phase	71.60 ± 0.3	1.90 ± 0.2	6.90 ± 0.2	4.00 ± 0.2	15.00 ± 0.2	0.50	0.100	73.50	–	–	–	–

* Average content 25.6%.

signed values, a water-cooled barrier consisting of loop coolers was installed in the beginning of the cooling zone, and a melt-accelerating agent was introduced to the batch.

Thus, in the case of variations in the glass composition accompanied by the introduction of new types of materials in the conditions of continuous production, one should take into account the actual change in the glass melt basicity, which can be indirectly found from the variation in the content of bivalent iron in the glass. The complex effect of such technological parameters as an increase in glass basicity, the reducing potential of the batch, and the content of Fe_2O_3 in glass contribute to an increase in the fractional and absolute content of bivalent iron. As the content of the latter increases, the diathermancy of the melt sharply decreases, which causes negative consequences such as excessive fuel consumption, an increase in the thermal stress in the main roof of the furnace, increased probability of the roof burning through, and a possible decrease in the service life of the system.

A prerequisite for successful operation of the glass-melting furnace consists in keeping the absolute content of Fe(II) within strictly set limits, which can be accomplished by the introduction of an additional melt-accelerating agent and a correction of the content of oxidizers (reducers) in the batch composition.

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